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High-Spin, Five-Coordinate Cobalt(II) Complexes

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Preparation and characterization of Co(Et$_4$dien)X$_2$ (Et$_4$dien = HN[CH$_2$CH$_2$N(C$_2$H$_5$)$_2$]$_2$; X = Cl, Br, I, N$_3$, NCS) complexes are reported. Spectral and magnetic properties show that the complexes are high spin and five-coordinate in the solid state. Based on a ligand field model, an interpretation of the observed electronic spectra and magnetic moments is presented.

Introduction

Recent studies have provided several examples of high-spin, five-coordinate complexes of the first-row transition metal ions.[1-5] Electronic structural work has been pioneered by Ciampolini and his co-workers,[6-8] who have shown that a ligand field model adequately represents the electronic spectra of several of the Ni(II) and Co(II) complexes, including the approximately trigonal bipyramidal complexes [Co(Me$_6$tren)Cl]Cl and [Ni(Me$_6$tren)Cl]Cl.[9]

In order to delve deeper into electronic structural matters for five-coordinate systems, we have prepared a series of high-spin complexes of the type Co(Et$_4$dien)X$_2$, where X (=I, Br, Cl, N$_3$, NCS) provides a substantial variation in ligand field strength. We have previously reported the results of a crystal and molecular structural determination of Co(Et$_4$dien)Cl$_2$.[10] In this paper, we present an interpretation of the electronic spectral and magnetic properties of these complexes in terms of a ligand-field model of electronic energy levels.

Experimental Section

Reagents.—All metal salts were reagent grade and were used without further purification. The ligand HN[CH$_2$CH$_2$N(C$_2$H$_5$)$_2$]$_2$ (Et$_4$dien) was obtained from K & K Chemical Co. and was used without further purification.

Preparation of Co(Et$_4$dien)X$_2$ (X = Cl, Br, I, N$_3$, NCS).—Anhydrous CoX$_2$ (0.01 mol) was dissolved in 200 ml of boiling methanol. The Et$_4$dien ligand (0.012 mol) was added slowly to the above solution with continuous stirring. The solution was filtered while hot. Addition of 75 ml of 1-butanol followed by evaporation of the methanol *in vacuo* gave the desired complex. *Anal.* Calcd for Co(Et$_4$dien)Cl$_2$: C, 41.74; H, 8.41; N, 12.17; Cl, 20.58. Found: C, 42.11; H, 8.39; N, 12.23; Cl, 20.12. Calcd for Co(Et$_4$dien)Br$_2$: C, 33.25; H, 6.70; N, 9.69; Br, 36.80. Found: C, 33.40; H, 6.61; N, 9.48; Br, 36.99. Calcd for Co(Et$_4$dien)I$_2$: I, 48.20; C, 27.20; N, 7.96; H, 5.49. Found: I, 48.37; C, 27.11; N, 7.92; H, 5.35. Calcd for Co(Et$_4$dien)(N$_3$)$_2$: C, 40.30; H, 8.11; N, 35.20. Found: C, 40.45; H, 8.15; N, 35.09. Calcd for Co(Et$_4$dien)(NCS)$_2$: C, 43.30; H, 7.44; N, 17.95; S, 16.40. Found: C, 43.80; H, 7.33; N, 17.98; S, 16.20.

Physical Measurements.—Absorption spectra were recorded on a Cary 14 spectrophotometer using cells of 1-cm path length. Spectral grade solvents were used as received. Magnetic susceptibilities were measured by the Gouy method, using solid Hg[Co(NCS)$_4$] and nickel chloride solutions as calibrants.[11] Conductivities were determined on an Industrial Instruments bridge, Model RC16B2, using a cell calibrated with 0.010 *M* KCl solution.

Results

Electronic spectra in Nujol mulls and in different organic solvents are set out in Table I. Conductance data and magnetic moments are given in Table II. The physical properties of the complexes Co(Et$_4$dien)X$_2$ (X = Br, NCS, N$_3$) are very similar to those observed[5] for Co(Et$_4$dien)Cl$_2$. The complexes are paramagnetic in the solid state and exhibit electronic absorption spectra which consist of three absorption regions centered at about 11,000, 15,000, and 20,000 cm^{-1}; in a variety of solvents, they have low molar conductances and their spectral and magnetic properties are essentially the same as observed in the solid state. We conclude, therefore, that all of the complexes under discussion are five-coordinate both in the solid state and in the solutions investigated.

Conductance and magnetic data for Co(Et$_4$dien)I$_2$ are given in Table III; spectral data are in Table IV. The complex Co(Et$_4$dien)I$_2$ is paramagnetic in the solid (4.8 BM) and presumably is five-coordinate because it exhibits an electronic absorption spectrum similar to that of the Co(Et$_4$dien)Cl$_2$ complex. The complex is paramagnetic in solution and exhibits different molar conductances and magnetic moments in different organic solvents. The electronic absorption spectra are also solvent dependent and in polar organic solvents are different from the spectrum observed in the solid state, as will be discussed later.

Ligand Field Model.—The crystal and molecular structure of the complex Co(Et$_4$dien)Cl$_2$ has shown that the coordination geometry does not possess any symmetry and that the molecule belongs to the point group C$_1$.[10] However, it is significant that spectral and magnetic properties of the complexes Co(Et$_4$dien)X$_2$ and [Co(Me$_6$tren)X]X are strikingly similar, particu-

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(9) The ligand Me$_6$tren is N[CH$_2$CH$_2$N(CH$_3$)$_2$]$_3$.

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TABLE I

ELECTRONIC SPECTRAL DATA FOR $Co(Et_4dien)X_2$ COMPLEXES[a]

$10^{-3}\nu_{max}$, cm^{-1} (ϵ_{max})					
Nujol	Ethanol	Acetone	Acetonitrile	DMF	Methylene chloride
$Co(Et_4dien)Cl_2$					
10.5	11.2 (18)	10.65 (18)	11.0 (18)	22.36 (18)	
15.2	15.4 (58)	15.3 (80)	15.3 (70)	15.2 (55)	
19.2	18.4 (60)	17.6 (Sh)	17.6 (Sh)	18.3 (60)	
	19.05 (60)	18.3 (60)	18.4 (65)	19.2 (50)	
	20.3 (sh)	19.2 (58)	19.2 (55)	20.3 (50)	
		20.3 (sh)	20.3 (sh)		
$Co(Et_4dien)Br_2$					
10.5			10.7 (15)	10.8 (15)	
15.2			15.25 (80)	15.25 (70)	
19.0			17.66 (75)	17.6 (70)	
			18.95 (sh)	18.9 (60)	
			19.8 (80)	19.8 (80)	
$Co(Et_4dien)(N_3)_2$					
12.4			12.45 (18)	12.5 (20)	
15.4			15.4 (75)	15.45 (80)	13.15 (30)
19.1			19.15 (65)	19.2 (70)	16.0 (120)
20.15			20.2 (70)	20.2 (70)	20.0 (100)
$Co(Et_4dien)NCS)_2$					
13.1			13.15 (30)	13.15 (30)	~5.0 (40)
15.9			15.9 (100)	16.0 (120)	13.15 (30)
20.0			20.0 (100)	20.0 (100)	16.0 (120)
21.0			21.0 (90)	21.1 (100)	20.0 (100)
					21.1 (100)

[a] All solutions were 0.01 *M* in complex; spectral data were obtained at room temperature.

TABLE II

MAGNETIC AND CONDUCTANCE DATA FOR THE $Co(Et_4dien)X_2$ COMPLEXES

	μ_{eff}, BM[a]				
Compound	Solid	Ethanol soln	Acetonitrile soln	Acetone soln	DMF soln
$Co(Et_4dien)Cl_2$	4.71	4.72 (14)[b]	4.70 (14)[b]	*c* (10)[b]	4.71 (18)[b]
$Co(Et_4dien)Br_2$	4.76	4.75 (16)	4.77 (12)	*c* (9)	4.77 (16)
$Co(Et_4dien)(N_3)_2$	4.64	4.63 (3)	4.64 (7)	*c* (2)	4.64 (9)
$Co(Et_4dien)(NCS)_2$	4.54	4.53 (4)	4.53 (5)	*c* (4)	4.54 (7)

[a] Measurements were made at 20–23°; spectral grade solvents were used. [b] Λ values in cm^2 $mole^{-1}$ ohm^{-1} are in parentheses; all conductance measurements were made at 28° on 0.0005 *M* solutions. [c] Magnetic moment was not measured.

TABLE III

MAGNETIC AND CONDUCTANCE DATA FOR $Co(Et_4dien)I_2$

Solvent	Λ, cm^2 $mole^{-1}$ ohm^{-1} [a]	μ_{eff}, BM[b]
Nujol		4.84
Acetonitrile	90	4.10
DMF	140	*c*
Chloroform	2	4.50
Methylene chloride	2	4.51

[a] All measurements were made at 25° on 0.0005 *M* solutions. [b] All measurements were made at 20–23°. [c] Not measured.

TABLE IV

ELECTRONIC SPECTRAL DATA FOR $Co(Et_4dien)I_2$

Solvent	ν_{max}, cm^{-1} (ϵ_{max})
Acetonitrile	12,650 (20), 15,150 (sh), 16,400 (80), 18,200 (sh), 20,800 (80)
DMF	16,250 (10), 19,600 (90), 21,050 (sh)
Chloroform	9500 (10), 14,200 (sh), 15,000 (290), 15,720 (sh), 16,600 (sh), 19,300 (96)
Methylene chloride	9500 (20), 14,300 (sh), 15,000 (320), 15,800 (sh), 16,600 (sh), 19,300 (110)
Nujol	10,100, 14,700, 15,500 (sh), 17,170, 18,100, 19,650

larly in view of the fact that the latter complex has been shown to possess C_3 symmetry (the coordination geometry is approximately C_{3v}).[12] This comparison suggests very strongly that for high-spin, five-coordinate complexes containing similar ligands, the *key electronic structural properties do not depend critically on the exact geometry of the molecule.* A similar conclusion has been reached from studies of high-spin Ni(II) complexes, because large deviations from both tetrahedral and octahedral geometries do not affect significantly the electronic spectra.[13] Thus, for the sake of simplicity, we will base our discussion of the spectral and magnetic properties of the $Co(Et_4dien)X_2$ complexes on a ligand field model that assumes D_{3h} symmetry.

The gaseous Co(II) ion has a ^4F ground state and some 15,000 cm^{-1} above it a ^4P ground state. In a trigonal-bipyramidal ligand field, the ground term is split into the states $^4A_2'$, $^4A_1''$, $^4A_2''$, $^4E''$, and $^4E'$; the ^4P term is split into $^4A_2'$ and $^4E''$. The relative energies of these states have been estimated by Ciampolini and co-workers on the basis of calculations using a point dipole model.[8] A qualitative energy level diagram based on the relative energies obtained by Ciampolini for ligand field strengths of the order found in $Co(Me_6tren)Cl^+$ is shown in Figure 1. We will make use of this energy level diagram for the interpretation of the spectral and magnetic properties of the $Co(Et_4dien)X_2$ complexes.[14]

Electronic Spectra of $Co(Et_4dien)X_2$.—Referring to Figure 1, we might expect to observe five spin-allowed transitions. As was pointed out earlier, the electronic spectra of the $Co(Et_4dien)X_2$ complexes consist of three absorption regions centered at about 11,000, 15,000, and 20,000 cm^{-1}. In addition, $Co(Et_4dien)(NCS)_2$ exhibits another band, at approximately 5000 cm^{-1}. Since the N-bonded thiocyanate ion exerts the strongest ligand field in this series of complexes, it is clear that this band should occur at lower energy for the other members of the series. Unfortunately, these bands could not be observed on our spectrophotometer owing to experimental difficulties. We thus assign the band at 5000 cm^{-1} to the $^4A_2'(F) \rightarrow {}^4E''(F)$ transition.[15] From the calculations performed by Ciampolini,[8] it is apparent that the energy separation between the two levels $^4A_2'(F)$ and $^4A_2'(P)$ is not very sensitive to the strength of the ligand field. Furthermore, since the two states are orbitally nondegenerate, they cannot split when the symmetry of the molecule is lower than D_{3h}. Thus, we expect the

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(13) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1957).

(14) In complexes where the degree of covalency is small, that is, where both interelectronic-repulsion and spin–orbit coupling parameters are not reduced considerably from free-ion values, a model based on ligand field theory is quite adequate for the interpretation of spectral and magnetic properties. This type of a model is applicable in particular to high-spin complexes containing chelating agents with light donor atoms where the interelectronic-repulsion parameters are very close to free-ion values. We will show that ligand field theory accounts quite successfully for the observed spectral and magnetic properties of the five-coordinate, high-spin complexes $Co(Et_4dien)X_2$.

(15) It is also possible that this band is due to the transitions to the accidentally degenerate $^4A_1''$ and $^4A_2''$ states.

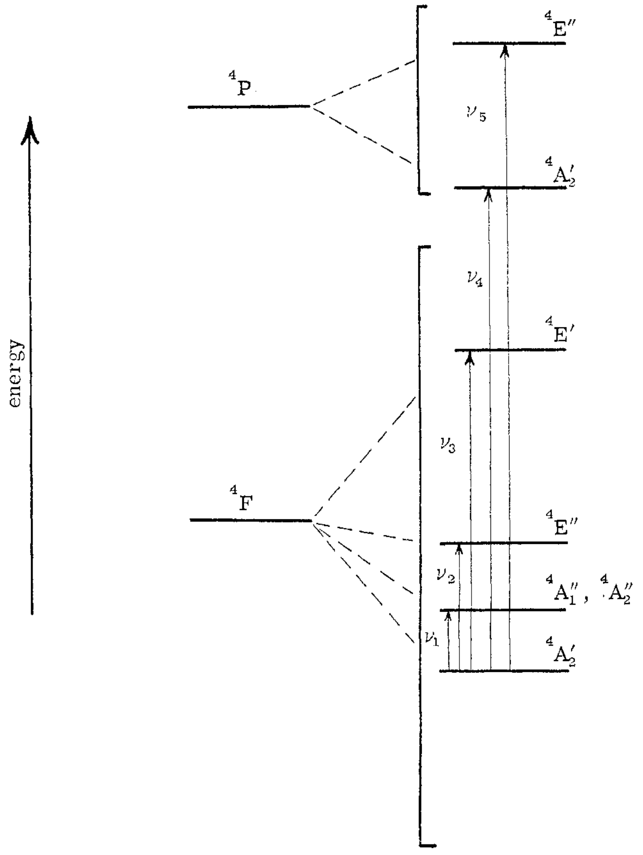

Figure 1.—Energy level diagram for an idealized $Co^{II}L_5$ complex of D_{3h} symmetry. Relative energies are displayed at a point in ligand field strength roughly comparable to that expected for $Co(Et_4dien)X_2$ complexes.

$A^4{}_2'$(F) → $^4A_2'$(P) transition to change by only a small amount when the ligand field strength is changed and the band should have a symmetrical shape. In fact, this is precisely what we observe for the band located at 15,000 cm^{-1}. We, therefore, assign this band to the $^4A_2'$(F) → $^4A_2'$(P) transition. A very similar situation occurs in tetrahedrally coordinated Co(II) and Ni(II) where the intense transition in the visible region is always correlated with the ^4F → ^4P and ^3F → ^3P free-ion transitions, respectively. Finally, we associate the band at 11,000 cm^{-1} with the $^4A_4'$(F) → $^4E'$(F) transition and the band system at 20,000 cm^{-1} with the $^4A_2'$(F) → $^4E''$(P) transition. A summary of the assignments for all the $Co(Et_4dien)X_2$ complexes is given in Table V.

The excited $^4E'$(F) and $^4E''$(P) levels must split in the lower symmetry offered by $Co(Et_4dien)X_2$ complexes. In a favorable case, either or both of the bands might resolve into their two components, and, in fact, for each of the complexes $Co(Et_4dien)(NCS)_2$ and $Co(Et_4dien)(N_3)_2$, the band system at 20,000 cm^{-1} is resolved into distinct "double" maxima located at 19,200, 20,200 cm^{-1} and 20,000, 21,000 cm^{-1}, respectively. It thus appears that the proposed energy level scheme reproduces the main features of the electronic spectra of the $Co(Et_4dien)X_2$ complexes. One very important feature of this scheme is the fact that the energy separation between the ground state and the low-lying $^4E''$ excited state is quite small ($\sim$5000 cm^{-1}), and this, of course, is quite evident on examining the magnetic properties of these complexes.

TABLE V

COMPARISON OF POSITIONS OF EXCITED STATES IN $Co(Et_4dien)X_2$ COMPLEXES[a]

	$^4A_2'$ →			
Complex	$^4E''$(F)	$^4E'$(F)	$^4A_2'$(P)	$^4E''$(P)
$Co(Et_4dien)I_2$	(3300)[b]	10,100	14,700 (15,500 sh)	17,170 18,100 19,650
$Co(Et_4dien)Br_2$	(3860)[b]	10,500	15,200	19,000
$Co(Et_4dien)Cl_2$	(4000)[b]	10,500	15,200	19,200
$Co(Et_4dien)(N_3)_2$	(4350)[b]	12,400	15,400	19,100 20,150
$Co(Et_4dien)(NCS)_2$	5000[c]	13,100	15,900	20,000 21,000

[a] Energies in cm^{-1} for spectra in Nujol mulls, except as indicated. [b] Calculated from eq 1; see text. [c] Methylene chloride solution.

Magnetic Properties of $Co(Et_4dien)X_2$.—The $^4A_2'$ ground state of the molecule is orbitally nondegenerate, and therefore to a first approximation the magnetic moments of these complexes should have the "spin-only" value for three unpaired electrons (3.88 BM). However, the data in Table II show that the $Co(Et_4dien)X_2$ complexes all have moments in excess of 3.88 BM by 0.6–1.0 BM. The higher values for the observed moments are logically due to a combination of second-order Zeeman terms (TIP) and an orbital contribution due to a mixing of ground and higher terms under spin–orbit coupling. From studies[8] of the temperature dependence of the susceptibility it appears that at room temperature the TIP contribution is an order of magnitude smaller than the orbital contributions for high-spin, five-coordinate complexes. Thus we shall assume that the observed moments μ_{obsd} follow

$$\mu_{obsd} = \mu_{so}\left(1 - \frac{K}{\Delta E}\right) \qquad (1)$$

where μ_{so} is the "spin-only" moment, K is a proportionality constant to be set from experimental data,[16] and ΔE is the energy of the $^4E''$ state, which is the lowest state that can be mixed with the ground state under spin–orbit coupling. In using eq 1, we assume that the dominant orbital contribution comes from the low-lying $^4E''$ state.

It follows that for a related series of complexes, the complex with ligands of highest field strength will exhibit the lowest magnetic moment. Furthermore, if ΔE is small to begin with, appreciable variations in the magnetic moment are expected as ΔE changes.

Referring to Table II, we can fix the value of K for the complex $Co(Et_4dien)(NCS)_2$, because the low-energy band $^4A_2''$ → $^4E''$ is observed at 5000 cm^{-1}. Thus, for the observed magnetic moment of 4.54 BM, K is equal to 850 cm^{-1}. As a check on this value, we

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(16) We resist the temptation to break down K into the form $k\lambda$, where k is a constant set by the nature of the ground and excited electronic configurations and λ is an "effective" spin–orbit coupling constant. The experimental data in the present case are not sufficiently detailed to merit any treatment more elaborate than the one given, because the TIP contribution remains an uncertainty.

calculate a magnetic moment of 4.46 BM for the complex [Co(Me$_6$tren)Cl]Cl, in good agreement with the observed[7] moment of 4.45 BM. The positions of the $^4E''$ states in the other Co(Et$_4$dien)X$_2$ complexes can now be estimated from eq 1. These values are reported in Table V.

Discussion

The ligand field interpretation of the spectral and magnetic properties of Co(Et$_4$dien)X$_2$ complexes is internally consistent. The observable band that depends most strongly on the nature of X is $^4A_2' \rightarrow {}^4E'$, as predicted. The spectrochemical order of ligands in high-spin, five-coordinate Co(II) complexes is NCS > N$_3$ > Cl > Br > I, which is the same as observed for tetrahedral Co(II) complexes.[17] In addition, the orbital contribution to the magnetic moment decreases as the field strength of X increases, as expected from theory.

We now turn to the stability of the five-coordinate structure as X is varied. For X = Cl, Br, NCS, and N$_3$, the five-coordinate structure appears to predominate in the solid state and in a variety of polar organic solvents. The structure of Co(Et$_4$dien)Cl$_2$, however, shows[10] that the Co–Cl bonds are quite strained and we would expect there to be a limit to the size of the X group that would give a five-coordinate structure. The Co(Et$_4$dien)I$_2$ complex apparently is an example where the steric factor against five-coordination is so large that outside of the solid state a variety of structural alternatives is more favorable.

For example, in DMF solution the complex is a 2:1 electrolyte and exhibits an electronic absorption spectrum typical of Co(II) in octahedral coordination.[18] The absence of low-energy charge-transfer bands indicates the dissociation of the two iodide ions in agreement with the high molar conductance. We suggest that the complex is logically formulated as Co(Et$_4$dien)(DMF)$_3$$^{2+}$. Independent evidence for this formulation is the fact that in DMF solution the spectra of Co(Et$_4$dien)(ClO$_4$)$_2$ and Co(Et$_4$dien)I$_2$ are identical.

In chloroform and methylene chloride solutions the Co(Et$_4$dien)I$_2$ complex is a nonelectrolyte and exhibits electronic absorption spectra quite typical of tetrahedrally coordinated Co(II). We, therefore, suggest that in these solvents the Et$_4$dien ligand acts as a bidentate ligand and that the complex in solution has a distorted tetrahedral geometry. The magnetic moment of 4.50 BM agrees well with this formulation.[17]

The molar conductance of the Co(Et$_4$dien)I$_2$ complex in acetonitrile suggests that the complex is a 1:1 electrolyte. That one iodide remains coordinated to the cobalt atom is evident from the presence of low-energy charge-transfer bands. The electronic absorption spectrum is quite different from the one observed for a solid sample of Co(Et$_4$dien)I$_2$. Furthermore, the spectrum cannot be associated with either a tetrahedral or an octahedral coordination for Co(II). Thus the complex most probably is either a distorted square-planar Co(Et$_4$dien)I$^+$ [19] or a five-coordinate species Co(Et$_4$dien)(CH$_3$CN)I$^+$.[20] Investigations aimed at the elucidation of the structure of this interesting new high-spin complex are underway in our laboratory.

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(19) Recall that in the series Ni(Et$_4$dien)X$_2$ the square-planar form Ni(Et$_4$dien)X$^+$ becomes increasingly favored over the five-coordinate structure in solution in the order Cl$^-$ < Br$^-$ < I$^-$.[5] In acetone, for example, where Ni(Et$_4$dien)Cl$_2$ exists predominantly as a five-coordinate high-spin complex, Ni(Et$_4$dien)I$_2$ exists primarily as square-planar Ni(Et$_4$dien)I$^+$,I$^-$. Thus, it is reasonable that in acetonitrile solution the Co(Et$_4$dien)I$_2$ complex is also present in the square-planar form Co(Et$_4$dien)I$^-$. If this structural analogy is accurate, then the magnetic crossover from a high-spin to a low-spin ground state, which takes place in going from five-coordinate [Ni(Et$_4$dien)I$_2$] to square-planar Ni(Et$_4$dien)I$^+$,I$^-$, is not observed in the transformation of Co(Et$_4$dien)I$_2$ to Co(Et$_4$dien)I$^+$. This would be explicable in terms of interelectronic-repulsion considerations which tend to favor a high-spin state in a d^7 structure (as compared with d^8).

(20) However, the low magnetic moment observed and the placement of the d–d bands are not readily interpretable on a five-coordinate model.